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## Determination of thermodynamic parameters of oxidative cleavage of gabapentin by N-Bromosacharin in presence of phosphotungstic acid in aqueous acetic acid medium

**Shahid Shafi Shah, Fairooz Ahmad Khan, Tariq Ahmad Khan, Umar Ali Dar, RK Bamzae and MU Khan**

### Abstract

Kinetic oxidation of Gabapentin by N-Bromosacharin in aqueous Acetic acid medium shows first order dependence on [NBSA], [Gabapentin]. The variation of  $[H^+]$  and [Sacharin] (Reaction product) has a remarked effect on the rate of reaction (rate decreases). Activation parameters for the reaction have been evaluated from Arrhenius plot by studying the reaction at different temperatures. The stoichiometry was found to be 1:1, and the products of oxidation were found to be Cyclic unsaturated Aldehyde ( $C_7H_{10}O$ ) and Ammonium acetate. The rate law has been derived on the basis of experimental Kinetic data and a plausible mechanism has been proposed.

**Keywords:**  $AcOH/CH_3COO-NH_4^+$ , Gabapentin, N-Bromosacharin, Phosphotungstic acid Sacharin

### Introduction

Oxidation of aminoacids with different oxidants have been a great deal attention in past years. The elucidation of reaction mechanism is still one of the most fascinating problems in inorganic and organic chemistry. Kinetics has furnished a pool of precious wealth of information about the nature and course of reaction <sup>[1]</sup> Viz molecularity, concentration, reaction path, frequency of activated complex, mass, temperature and other properties such as influence of substituent groups, rate equation, salt effect, isotopic effect, activation parameters and various environmental changes, like solvent polarity, PH, and catalytic changes in a reaction. The given study leads to work at stoichiometry, identification of intermediates and isolation of end products as an indirect support to reaction mechanism. The versatile nature of N-halo compounds <sup>[2]</sup> is due to their ability to act as sources of halonium ions, hypo halite species and nitrogen anions, which act as both bases and nucleophiles. N-Bromosacharin (NBSA) is a potential oxidising agent. The kinetics and mechanistic investigation of the oxidation of Gabapentin (GBP) by various oxidising agents have been studied earlier, but there are no reports of oxidation of Gabapentin by N-Bromosacharin in presence of phosphotungstic acid. Hence the present work deals with the oxidation of Gabapentin by N-Bromosacharin in presence of phosphotungstic acid in aqueous acetic acid medium.

### Experimental

The solution of N-Bromophthalimide so obtained was prepared by dissolving its weighed quantity in 100%  $CH_3COOH$ (B.D.H) and kept either amber coloured flask or black paper wrapped around it to save it from the action of diffused day light which alters appreciably its concentration. The standardization of N-Bromophthalimide was done by taking one ml of its solution in conical flask to which 10 ml of 2% KI solution followed by 5 ml of 2N perchloric acid added to it. The liberated iodine was titrated against standard sodium thiosulphate solution using starch solution as indicator. Gabapentin (Sigma Aldrich) was used as a substrate for the preparation of solution, which was prepared in requisite volume of glacial acetic acid solution.

### Kinetic Measurement

The kinetic measurements were made under pseudo first order conditions, by keeping large excess of Gabapentin(GBP) over oxidant (N-Bromosacharin).

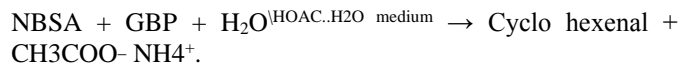
The known volume of Oxidant (NBSA), acetic acid, perchloric acid were taken in a conical flask, while substrate (GBP), and rest amount of water were taken in another flask. These two stoppered flasks were placed at experimental temperature  $\pm 0.1$  °C. After the equilibrium of temperature, the both solutions were mixed in presence of catalyst [PTA] and aliquot was withdrawn immediately and was quenched. The amount of unreacted N-Bromosacharin (NBSA) was estimated iodometrically with the help of standard solution of sodium thiosulphate using starch as an indicator.

The aliquots were withdrawn at regular intervals of time. The titre value at zero interval of time was taken as 'a', and at time 't' (a-x). The experimental data were fed into the integrated form of equation for first order reactions and Ostwald's isolation method [3] was used. The effect of perchloric acid, sacharin, Gabapentin, N-Bromosacharin, dielectric constant of the medium and [PTA] was investigated.

### Stoichiometry and product analysis

The stoichiometry of each reaction under study was determined under experimental conditions. The oxidation products of the reaction were identified chromatographically [4] and by spot test qualitatively [5]. The estimated amount of unreacted N-Bromosacharin showed that one mole of GBP consumes one mole of NBSA. The cyclo hexenal and Ammonium acetate were the end products. Different tests like Saturation tet, functional group test and melting point (171.1

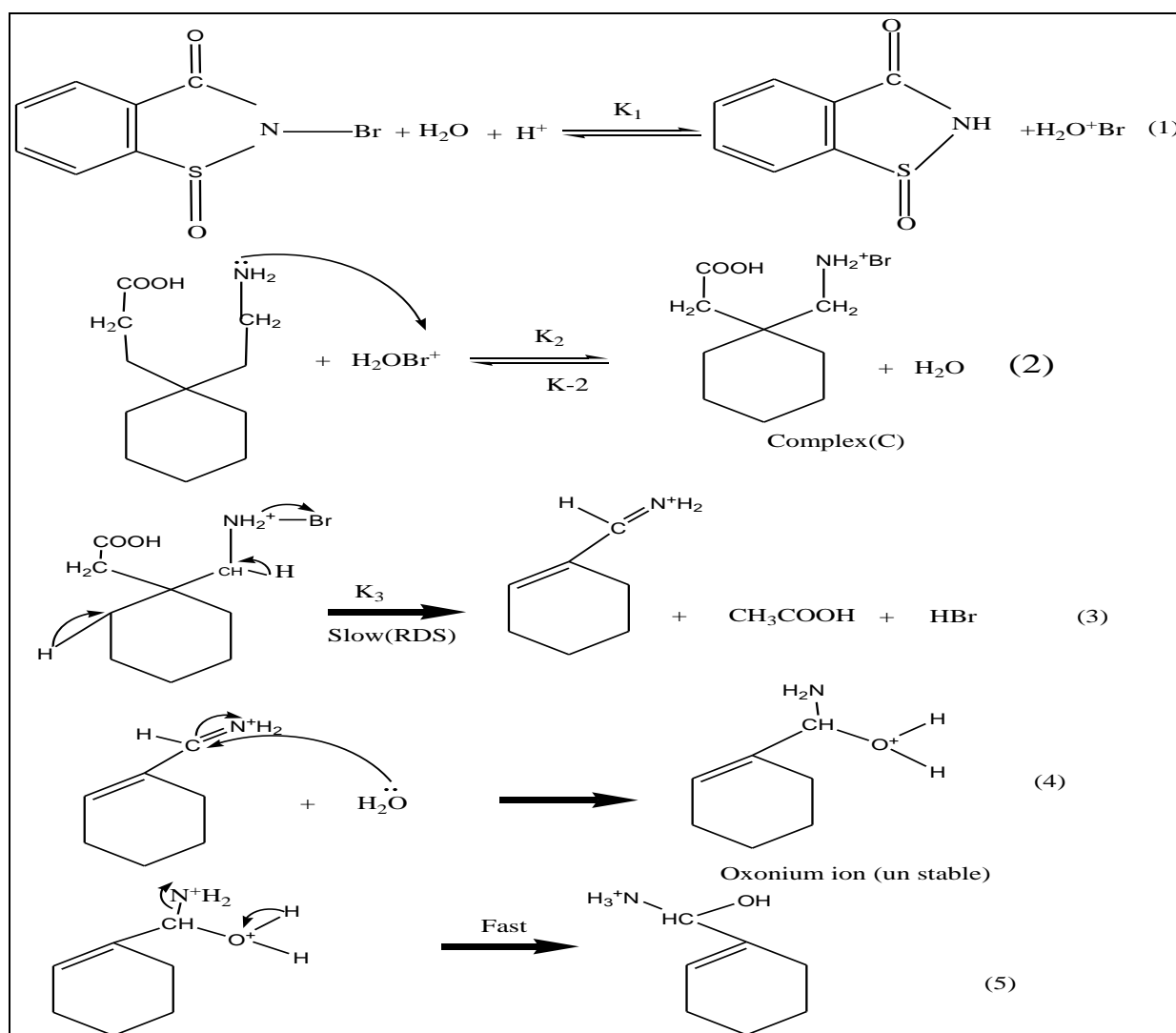
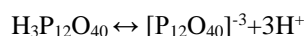
°C) reveals formation of cyclohexenal as the end product of oxidation. Similarly ammonium acetate formed was determined by separate test.

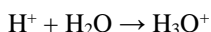
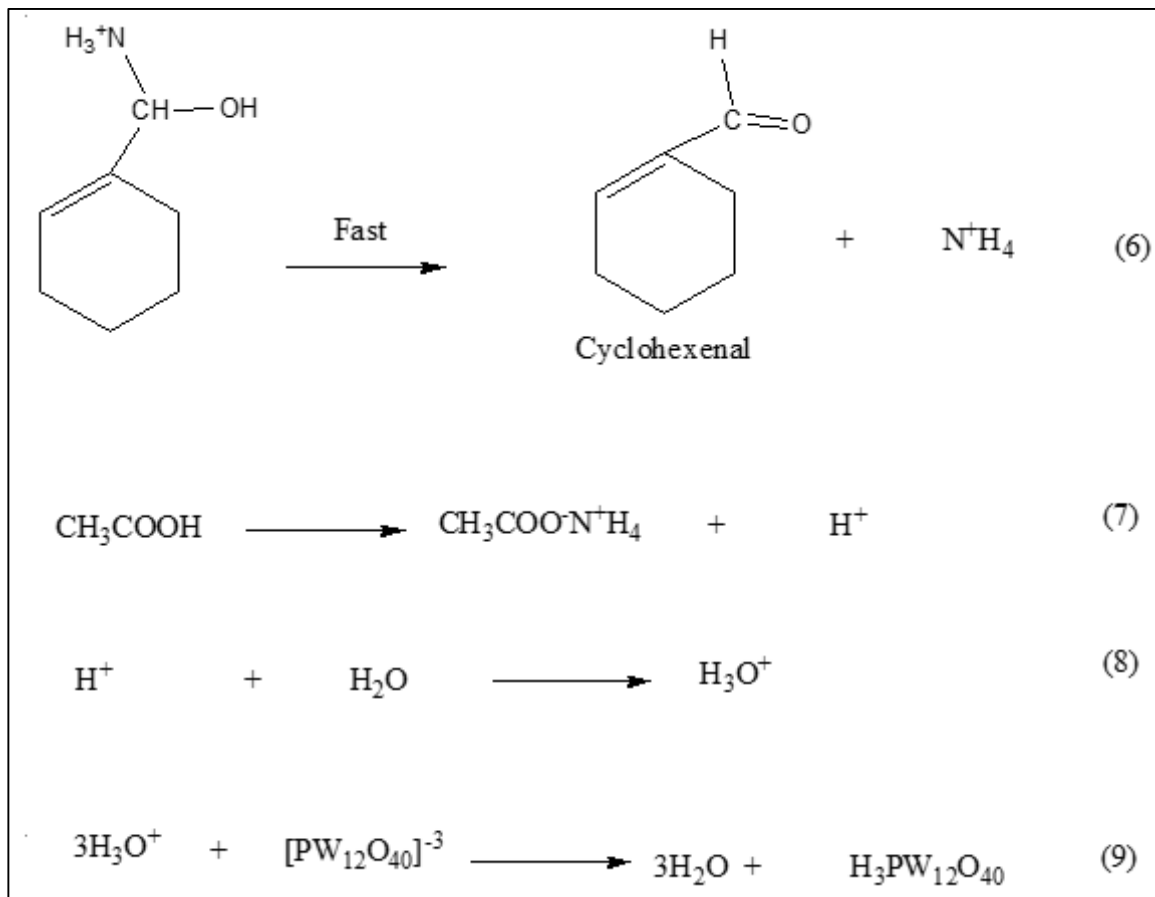


### Results and Discussion

The kinetics of Gabapentin by NBSA in varying percentage of acetic acid was carried at different temperatures under pseudo first order conditions. The plot of  $\log [\text{NBSA}]$  vs time was found to be linear. Pseudo first order rate was evaluated from the slope. The value of rate constant (K) increased with increase in the concentration of GBP. The plot of  $\log$  of K vs  $\log [\text{GBP}]$  was found linear indicating first order dependence with respect to the [GBP]. The value of rate constant decreases with increase in dielectric constant. The plot of  $\log k$  vs  $10^3/D$  was found linear with negative slope. The rate of the reaction decreased with increase in concentration of sachrin for the detection of radicals in the reaction mixture 1-2 ml of Acrylonitrile was added, the absence of turbidity revealed absence of free radicals by trapping method [6].

### Mechanistic path for the oxidation of Gabapentin by N-Bromosacharin





The phosphotungstic acid liberated is used to catalyse the fresh reaction.

Bacchawat and Mathur<sup>[7]</sup> developed NBSA a potential titrant for the oxidometric determination of some reductants in aqueous acetic acid medium.

**Rate law:** From the above-proposed mechanism, finally rate has been derived as: **kobs.** =  $K_1k_2k_3[\text{H}^+][\text{GBP}][\text{PTA}]/[\text{Sac.}]\{k_2+k_3\}$ ..... (8)

### Typical Kinetic Run

#### Plot of log a/ (a-x) vs. Time

Effect of [NBSA]: In presence of oxidant the concentration of products get increased

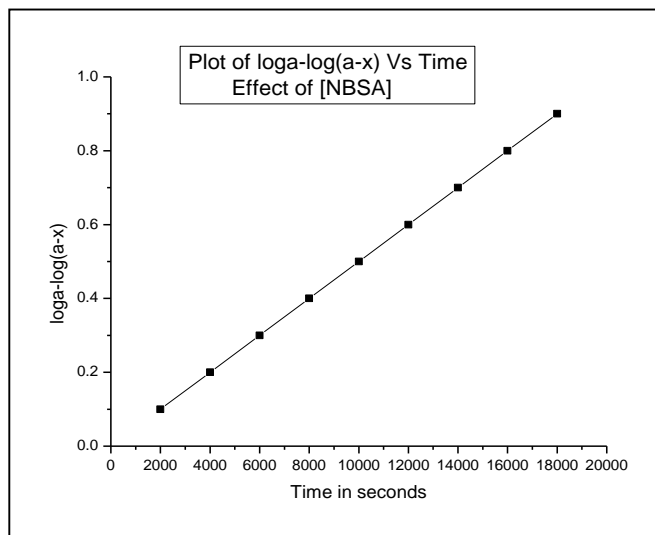
[NBSA]	:	2.50×10 <sup>-3</sup> (mol.dm <sup>-3</sup> )
[GBP]	:	1.25×10 <sup>-2</sup> (mol.dm <sup>-3</sup> )
[H <sup>+</sup> ]	:	1.25×10 <sup>-3</sup> (mol.dm <sup>-3</sup> )
HOAC-H <sub>2</sub> O	:	30% (V/V).
Temperature	:	308 K

**Table 1:** Variariation of rate constant with time

S. No	Time(sec)	Vol. of N/1000 hypo(ml)	10 <sup>5</sup> k <sub>1</sub> (S <sup>-1</sup> )
1	0	5.00	-
2	1800	4.20	9.69
3	3600	3.50	9.91
4	5400	3.00	9.46
5	7200	2.50	9.63
6	9000	2.15	9.38
7	10800	1.80	9.46
8	12600	1.50	9.55
9	14400	1.30	9.36
10	16200	1.10	9.35

Average K<sub>1</sub> = 9.55×10<sup>-5</sup>(S<sup>-1</sup>)

Graphical K<sub>1</sub> = 9.53×10<sup>-5</sup>(S<sup>-1</sup>)



**Fig 1:** Variariation of concentration of product with time

### Typical Kinetic Run

#### Plot of log a/ (a-x) vs. Time

Effect of [GBP]: The concentration of substrate get decreased with the course of time, and hence increases the product concentration.

[NBSA]	:	2.50×10 <sup>-3</sup> (mol.dm <sup>-3</sup> )
[GBP]	:	1.25×10 <sup>-2</sup> (mol.dm <sup>-3</sup> )
[H <sup>+</sup> ]	:	1.25×10 <sup>-3</sup> (mol.dm <sup>-3</sup> )

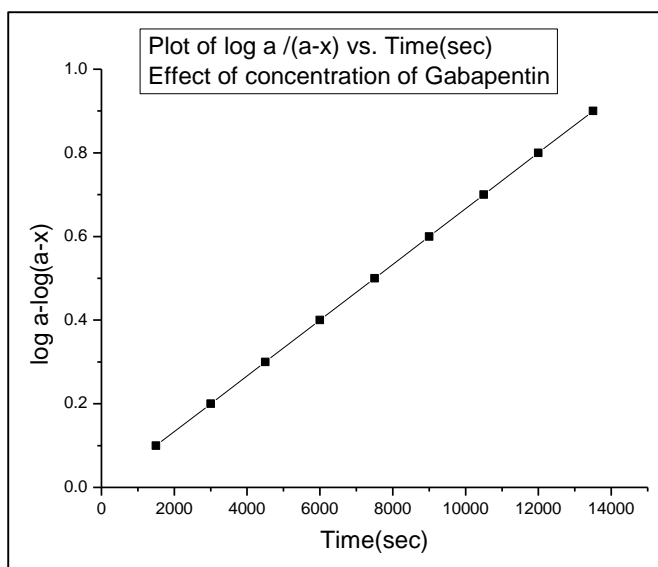
HOAC-H<sub>2</sub>O : 30% (V/V).  
 Temperature : 308 K

**Table 2:** The value of rate constant get decreased with with the course of time, because the concentration of substrate (GBP) get decreased with the course of time.

S. NO	Time(sec)	Vol. of N/1000 hypo(ml)	10 <sup>5</sup> k <sub>1</sub> (S <sup>-1</sup> )
1	0	5.00	-
2	1500	3.95	15.72
3	3000	3.15	15.40
4	4500	2.50	15.40
5	6000	2.00	15.27
6	7500	1.55	15.61
7	9000	1.25	15.40
8	10500	1.00	15.33
9	12000	0.80	15.27

Average K<sub>1</sub> = 15.42 × 10<sup>-5</sup>(S<sup>-1</sup>)

Graphical K<sub>1</sub> = 15.40 × 10<sup>-5</sup>(S<sup>-1</sup>)



**Fig 2:** From the figure it is clear that the concentration of products get increased with time.

### Typical Kinetic Run

#### Plot of log a/ (a-x) vs. Time

#### Effect of [Perchloric acid]

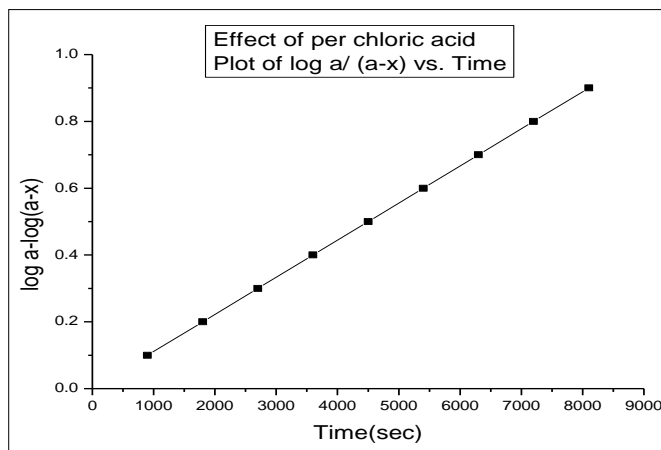
[NBSA] : 2.50 × 10<sup>-3</sup>(mol.dm<sup>-3</sup>)  
 [GBP] : 1.25 × 10<sup>-2</sup>(mol.dm<sup>-3</sup>)  
 [H<sup>+</sup>] : 1.25 × 10<sup>-3</sup>(mol.dm<sup>-3</sup>)  
 HOAC-H<sub>2</sub>O : 30% (V/V).  
 Temperature : 308 K

**Table 3:** Variations of rate constant by perchloric acid.

S. No	Time(sec)	Vol. of N/1000 hypo(ml)	10 <sup>5</sup> k <sub>1</sub> (S <sup>-1</sup> )
1	0	5.00	-
2	900	4.00	24.80
3	1800	3.20	24.80
4	2700	2.60	24.22
5	3600	2.05	24.77
6	4500	1.65	24.64
7	5400	1.35	24.25
8	6300	1.05	24.77
9	7200	0.85	24.61

Average K<sub>1</sub> = 24.62 × 10<sup>-5</sup>(S<sup>-1</sup>)

Graphical K<sub>1</sub> = 24.60 × 10<sup>-5</sup>(S<sup>-1</sup>)



**Fig 3:** Increase in concentration of perchloric acid increased the rate of reaction.

### Dependence of rate of oxidation reactions on the initial concentration of oxidant (NBSA)

As the concentration of oxidant get increased, the value of rate constant also increases.

[PTA] : 1.00 × 10<sup>-3</sup>(mol.dm<sup>3</sup>)  
 [NBSA] : Varried.  
 [GBP] : 1.25 × 10<sup>-2</sup>(mol.dm<sup>-3</sup>)  
 [H<sup>+</sup>] : 1.25 × 10<sup>-3</sup>(mol.dm<sup>-3</sup>)  
 HOAC-H<sub>2</sub>O : 30% (V/V).  
 Temperature : 308 K

**Table 4:** Variations of rate constant with variation in concentration of N-Bromosacharin.

[GBP] 10 <sup>-3</sup> (mol.dm <sup>-3</sup> )	[PTA] 10 <sup>-3</sup> (mol.dm <sup>3</sup> )	[NBSA] 10 <sup>3</sup> (mol.dm <sup>3</sup> )	10 <sup>5</sup> K <sub>1</sub> (S <sup>-1</sup> )
1.25	1.00	1.00	10.35
1.25	1.00	1.25	10.38
1.25	1.00	2.00	10.45
1.25	1.00	2.50	10.65
1.25	1.00	4.00	10.40
1.25	1.00	5.00	10.34

### Dependence of rate of oxidation on the concentration of Gabapentin

By increasing the concentration of substrate, (Gabapentin) the value of rate constant increased.

[PTA] : 1.25 × 10<sup>-3</sup>(mol.dm<sup>-3</sup>)  
 [NBSA] : 2.5 × 10<sup>-3</sup>(mol.dm<sup>-3</sup>)  
 [GBP] : Varried.  
 [H<sup>+</sup>] : 1.25 × 10<sup>-3</sup>(mol.dm<sup>-3</sup>)  
 HOAC-H<sub>2</sub>O : 30% (V/V).  
 Temperature : 308 K

**Table 5:** Variations of rate constant by varying the concentration of Gabapentin.

[NBSA] 10 <sup>-3</sup> (mol.dm <sup>-3</sup> )	[PTA] 10 <sup>-3</sup> (mol.dm <sup>-3</sup> )	[GBP] 10 <sup>-2</sup> (mol.dm <sup>-3</sup> )	10 <sup>5</sup> K <sub>1</sub> (S <sup>-1</sup> )
2.5	1.25	1.00	8.65
2.5	1.25	1.25	10.55
2.5	1.25	2.00	13.60
2.5	1.25	2.50	16.42
2.5	1.25	4.00	18.94
2.5	1.25	5.00	20.23

### Dependence of rate on the variation of perchloric acid:

It has been found that increase in concentration of perchloric acid increased the value of rate constant.

[PTA] :  $1 \times 10^{-2}(\text{mol}.\text{dm}^{-3})$   
 [NBSA] :  $2.5 \times 10^{-3}(\text{mol}.\text{dm}^{-3})$   
 [GBP] :  $1.25 \times 10^{-2}(\text{mol}.\text{dm}^{-3})$   
 [H<sup>+</sup>] : Varried.  
 HOAC-H<sub>2</sub>O : 30% (V/V).  
 Temperature : 308 K

**Table 6:** Varriation of rate constant by varying the concentration of perchloric acid.

[PTA] 10 <sup>-2</sup> (mol.dm <sup>-3</sup> )	[H <sup>+</sup> ]10 <sup>-3</sup> (mol.dm <sup>-3</sup> )	10 <sup>5</sup> K <sub>1</sub> (S <sup>-1</sup> )
1.00	1.00	8.60
1.00	1.25	9.85
1.00	2.00	12.88
1.00	2.50	15.33
1.00	4.00	21.96
1.00	5.00	26.07

**Dependence of rate on the di electric constant of the medium**

By increasing the value of di electric constant, the value of rate constant increased.

[PTA] :  $1.00 \times 10^{-2} \text{ mol}.\text{dm}^{-3}$   
 [NBSA] :  $2.5 \times 10^{-3}(\text{mol}.\text{dm}^{-3})$   
 [GBP] :  $1.25 \times 10^{-2}(\text{mol}.\text{dm}^{-3})$   
 [H<sup>+</sup>] :  $1.25 \times 10^{-2}(\text{mol}.\text{dm}^{-3})$   
 HOAC-H<sub>2</sub>O : varried  
 Temperature : 308 K

**Table 7:** Varriation of rate constant by varying the dielectric constant of the medium.

[PTA]10 <sup>-2</sup> mol.dm <sup>-3</sup>	HOAC-H <sub>2</sub> O%(V/V)	10 <sup>3</sup> /D	10 <sup>5</sup> K <sub>1</sub> (S <sup>-1</sup> )
1.00	20	17.17	8.99
1.00	30	19.15	10.55
1.00	40	21.98	11.46
1.00	50	25.64	12.96
1.00	60	30.36	16.03

**Dependence of rate on the concentration of Sacharin**

By increasing the concentration of saccharin the value of rate constant decreased.

[PTA] :  $0 \text{ mol}.\text{dm}^{-3}$   
 [NBSA] :  $2.5 \times 10^{-3}(\text{mol}.\text{dm}^{-3})$   
 [GBP] :  $1.25 \times 10^{-2}(\text{mol}.\text{dm}^{-3})$   
 [H<sup>+</sup>] :  $1.25 \times 10^{-2}(\text{mol}.\text{dm}^{-3})$   
 HOAC-H<sub>2</sub>O : 30%  
 Temperature : 308 K

**Table 8:** Showing the variation of rate constant with increase in concentration of saccharin.

[PTA] 10 <sup>-2</sup> (mol.dm <sup>-3</sup> )	[SA]10 <sup>-2</sup> (mol.dm <sup>-3</sup> )	10 <sup>5</sup> K <sub>1</sub> (S <sup>-1</sup> )
1.25	0	10.55
1.25	1.00	10.44
1.25	1.25	10.39
1.25	2.00	10.31

**Calculation of thermodynamic parameters**

Effect of temperature: The rate of reaction was studied at different temperatures to evaluate various activation parameters such as temperature coefficient, frequency factor, energy of activation, free energy of activation and enthalpy of activation and entropy of activation.

1 Temperature coefficient ( η):

$$\eta = K_2/K_1 \dots \dots \dots \text{eq (1)}$$

Where K<sub>1</sub> and K<sub>2</sub> are rate constants at temperatue T<sub>1</sub> and T<sub>2</sub> respectively.

**2 Energy of activation**

It can be calculated from Arhenious equation i.e

$$K = Ae^{-E_a/RT}$$

Slope = - E<sub>a</sub>/2.303R

$$E_a = 2.303RT_1T_2/(T_2 \dots T_1) \times \log K_2/K_1 \dots \dots \dots \text{eq (11)}$$

**3 Frequency factor**

It can be calculated as

$$\log A = \log K + E_a/2.303RT \dots \dots \dots \text{eq (111)}$$

**3 Free energy (Δ G)**

The value of free energy can be calculated as

$$-\Delta G = 2.303RT \log K \dots \dots \dots \text{eq (IV)}$$

Where K = K<sub>h</sub>/K<sub>b</sub> T

**4 Enthalpy of activation (ΔH)**

The enthalpy of activation was calculated from Errying equation by plotting log of Krh/KBT vs 1/T graphically. The slope of plot is Δ H/2.303R..

**5 Entropy of activation (ΔS)**

The entropy of activation can be calculated from the equation

$$\Delta G = \Delta H - T \Delta S \dots \dots \dots \text{eq (V)}$$

Hence it is concluded that the activation parameters viz E<sub>a</sub>, A, Δ H, Δ G and Δ S have been calculated which are given in the table.

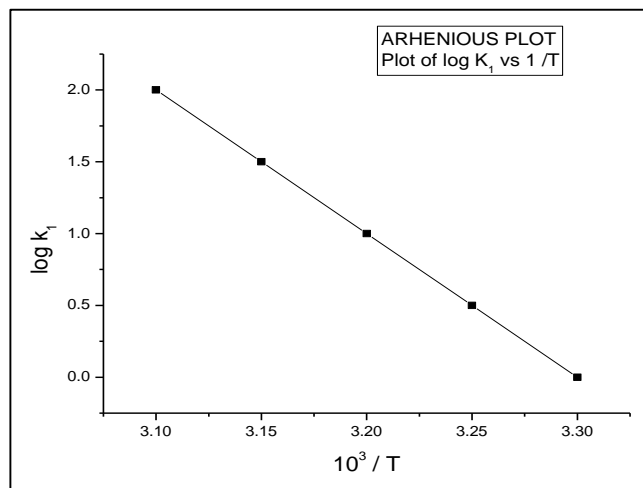
**Dependence of rate on the variation of temperature**

The value of rate constant was analysed at different temperatures and it was found that rate constant depends up on temperature.

[NBSA] :  $2.5 \times 10^{-3}(\text{mol}.\text{dm}^{-3})$   
 [GBP] :  $1.25 \times 10^{-2}(\text{mol}.\text{dm}^{-3})$   
 [H<sup>+</sup>] :  $1.25 \times 10^{-2}(\text{mol}.\text{dm}^{-3})$   
 HOAC-H<sub>2</sub>O : 30%  
 Temperature : varied.

**Table 9:** Varriation in the value of rate constant by varying temperature.

Temp.(K)	[PTA]10 <sup>2</sup> (mol.dm <sup>3</sup> )	10 <sup>5</sup> K <sub>1</sub> (S <sup>1</sup> )				
303	1.25	8.30				
308	1.25	10.55				
313	1.25	13.62				
318	1.25	16.57				
S. No	[GBP]10 <sup>-2</sup> (mol.dm <sup>3</sup> )	K <sub>35</sub> /K <sub>30</sub>	K <sub>40</sub> /K <sub>35</sub>	K <sub>45</sub> /K <sub>40</sub>	K <sub>40</sub> /K <sub>30</sub>	K <sub>45</sub> /K <sub>35</sub>
1	1.25	1.34	1.32	1.23	1.78	1.68



**Fig 5:** Plot of log k<sub>1</sub> vs 1 / T

The value of activation energy can be calculated from the slope of the plot, i.e.,

$$\text{Slope} = -E_a / 2.303 R$$

Further from the graphical value, the frequency factor (A) has been calculated. (eq 111, p.no.3).

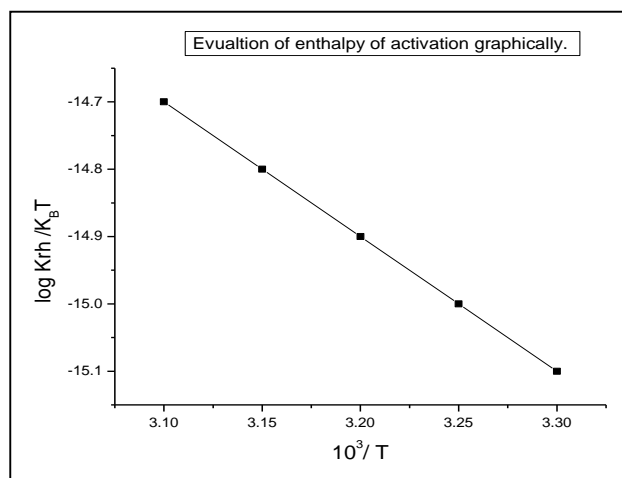


Fig 6: Variation of  $K_{rh} / K_B T$  and  $1/T$ .

The value of  $\Delta H$  can be calculated from the slope of the plot between  $K_{rh} / K_B T$  and  $1/T$  (fig 6), where  $k_r$  is the specific rate constant.

The value of  $\Delta G$  can be calculated from eq (1v), p.no.3

The value  $\Delta S$  can be calculated from eq (v), p.no.3.

All these above given parameters are given in the table below.

	Ea KJmol <sup>-1</sup>	A (S <sup>-1</sup> )	$\Delta H$ KJmol <sup>-1</sup>	$-\Delta G$ KJmol <sup>-1</sup>	$\Delta S$ JKmol <sup>-1</sup>
GBP	67.46 ± 0.29	$5.34 \times 10^3$ ± 0.84	69.54 ± 0.26	-88.29 ± 0.18	-105.68 ± 0.44

#### Dependence of rate of reaction on concentration of PTA:

By increasing the concentration of PTA, the value of rate constant get increased. It is given in the figure 7

Table 10: Experimental kinetic data.

[GBP]10 <sup>-2</sup> (mol.dm <sup>3</sup> )	[NBSA]10 <sup>-3</sup> (mol.dm <sup>3</sup> )	[H <sup>+</sup> ]10 <sup>-2</sup> (mol.dm <sup>3</sup> )	[HOAC- H <sub>2</sub> O] %	K×10 <sup>5</sup> S <sup>-1</sup>	[PTA] 10 <sup>-2</sup> (mol.dm <sup>3</sup> )
1.25	1.00	2.00	30	10.35	1.00
1.25	1.25	2.00	30	10.42	1.00
1.25	2.00	2.00	30	10.45	1.00
1.25	2.50	2.00	30	10.65	1.00
1.25	4.00	2.00	30	10.42	1.00
1.25	5.00	2.00	30	10.34	1.00
1.00	2.50	2.00	30	8.65	0
1.25	2.50	2.00	30	10.55	0
2.00	2.50	2.00	30	13.60	1.25
2.50	2.50	2.00	30	16.42	1.25
4.00	2.50	2.00	30	18.94	1.25
5.00	2.50	2.00	30	20.23	1.25
1.25	2.50	1.00	30	8.60	1.25
1.25	2.50	1.25	30	9.85	1.50
1.25	2.50	2.00	30	12.88	1.50
1.25	2.50	2.50	30	15.33	1.50
1.25	2.50	4.00	30	21.96	2
1.25	2.50	5.00	30	26.07	2
1.25	2.50	2.00	20	7.99	0
1.25	2.50	2.00	30	11.65	2.5
1.25	2.50	2.00	40	12.46	2.5
1.25	2.50	2.00	50	13.96	2.5
1.25	2.50	2.00	60	15.03	2.5

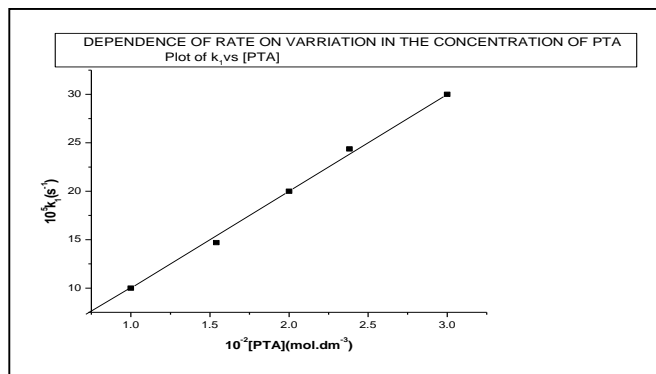


Fig 7: Dependence of rate in the variation of concentrations of PTA

#### Conclusion

Kinetic studies utilizing NBSA as an oxidant in series of reaction lead us to conclude that the activity of it is much limited and needs to be explored in a broad way. The study will act as a mile stone and will pay the way for future researcher to enlighten the mechanism for the oxidation of organic compounds like disulphides, acetophenone, amines and amino acids. Its applied aspects may be judged in lather industries<sup>[8,9]</sup>, analytical, chemical separation, paper and pulp industries<sup>[10]</sup>.

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